Evaluation of Treatment Options to Reduce Water-Borne Selenium at Coal Mines in West-Central Alberta

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Microbial Technologies, Inc

MICROBIAL
TECHNOLOGIES

Evaluation of Treatment Options to Reduce Water-Borne Selenium at Coal Mines in West-Central Alberta

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Executive Summary

Microbial Technologies, Inc. reviewed the environmental chemistry of selenium and technologies for its treatment at three mountain coal mines in West-Central Alberta. These mines have recently been shown to release selenium to adjacent water bodies, resulting in its uptake into the food chain.

Based on limited data from the Alberta mines, selenium is found in the dissolved form (mostly as selenate) in surface waters, a form that from a chemical perspective is relatively unreactive. Selanate can be reduced to selenite, a form more readily removed (chemically) from solution, or (biologically) to elemental selenium, an insoluble form. Currently, the expected duration of selenium release at the Alberta coal mines is not known.

Notwithstanding the advantages or disadvantages of treatment technologies, preventative measures such as submerging seleniferous sulphides or covering waste rock are recognized as an integral component of any management plan for selenium at coal mines in West-Central Alberta. These measures are not fully reviewed in this document. However, a manual of Best Management Practices for seleniferous mining wastes is currently being developed in Idaho and is expected to provide practical guidance with regards to such preventative measures.

Eleven technologies were reviewed in detail. These include physically-based technologies (reverse osmosis, nanofiltration, and ion exchange), chemically-based technologies (iron precipitation and catalyzed cementation), and biologically-based technologies (algal volatilization, biological treatment plant, in-situ treatment, Biopass and other passive treatment systems, treatment wetlands, and evaporation ponds). Several of these technologies have been tested at a pilot-scale or implemented as treatment facilities.

The above technologies varied considerably with regards to their ability to remove selenate from solution cost-effectively. Several of them could not meet a treatment objective of 5 µg/L. Treatment costs ranged from less than USD$1.00/1,000 gallons for in-situ treatment to over $10.00/1,000 gallons for reverse osmosis and iron precipitation. Some technologies employ very straightforward processes, with simple process flowsheets (e.g., in-situ treatment or constructed wetlands), whereas others rely on more complex processes (e.g., iron precipitation). In addition, some technologies are handicapped by the necessity to manage residues from treatment, such as brines or wash solutions for membrane filtration and ion exchange, or sludges resulting from iron precipitation.

These different technologies were evaluated using a scoring system based on nine separate factors relevant to coal mines in West-Central Alberta. Two technologies stood out from the others as being most suited: in-situ treatment and bioreactors (biological treatment plant). Four other technologies might possibly be appropriate to some of the sites if favoured by some site-specific factors: reverse osmosis, nanofiltration, the Biopass/passive treatment systems and treatment wetlands. The other technologies were deemed too underdeveloped or inappropriate for application at coal mines in West-Central Alberta.

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1 Introduction

Concerns about selenium (Se) toxicity were galvanized by its effects observed in the Kesterson Reservoir, San Joaquin Valley, California. Field studies in the early 1980's documented dramatic losses in migratory bird populations and specifically attributed to Se the decline in reproduction of waterfowl, shorebirds and other aquatic birds (1). One other case of Se ecotoxicity had already been documented earlier at Belews Lake, and more reservoirs exhibiting impacts from Se were identified later on, indicating that this was not an isolated incident. Se ecotoxicity in aquatic ecosystems was thus uncovered as a new ecological problem.

Although knowledge of Se poisoning of cattle had existed for some time (2), the striking finding following these new environmental disasters was that ecotoxicity occurred at very low Se concentrations. Little was known about how it acted at such low doses, and this prompted an accelerated program of investigation to understand its fate and behavior in aquatic ecosystems and its toxicological mode of action. Although much has since been learned about its ecotoxicity, there are still knowledge gaps, particularly for cold water environments - compared to warm water environments.

Monitoring data in the late1990's indicate that selenium concentrations have increased in surface waters downstream from mountain coal mines in West-Central Alberta (3). This is a problem that appears to be specific to coal mines in the upper McLeod and Smoky river basins. This study confirmed that selenium concentrations exceeded the Canadian and US-EPA water quality guidelines for the protection of freshwater aquatic life (i.e., 1 and 5 ug Se/L, respectively) in various streams and one end pit lake influenced by active coal mines. In contrast, selenium was usually below the most stringent guideline (i.e., Canadian or CCME) at the reference sites. Moreover, selenium in fish muscles and eggs was significantly more elevated at sites impacted by coal mines compared with reference sites (except for one reference site). This survey also showed selenium is elevated in fish tissues from sites downstream of the mines, compared to reference sites. Concurrent monitoring at the mines confirmed the above findings of elevated selenium in waters draining coal mines (4). Background or upstream Se concentrations in water bodies draining the mines averaged 0.7 µg/L (N=56) compared with 9.1 µg/L (N=126) at downstream sampling stations. Se concentrations in end pit lakes, rock dump springs, and settling pond effluents averaged 19.8, 115, and 42.7 µg/L, respectively, well above the water quality guidelines. Long-term temporal trends for selenium loadings or subsequent selenium concentrations in water bodies influenced by the mines is not currently known.

Based on available data, lowest selenium concentrations in streams occurred in the spring compared to summer and fall. Lower concentrations in spring may be due a dilution effect from snowmelt and runoff. Limited data for chemical speciation of selenium indicated that it was present mostly in the dissolved form (as selenate).

Elevated selenium in surface waters of western North America have been associated with various activities including irrigation of seleniferous soils, and at phosphate and coal mines in Idaho, Wyoming and British Columbia (e.g., 2, 3, 10). Geological sources particularily Cretaceous marine shales appear to be an important source of selenium in these areas. Elevated selenium in surface waters has also been associated with gold deposits and is occasionally a problem at gold mines. Gold mine effluents that contain selenium typically also contain other contaminant, such as ammonium, arsenic, cyanide, and nitrate (e.g., Zortman-Landusky Mines, Gilt Edge), and possibly antimony and mercury. This is important because the problems – and solutions – associated with selenium treatment for gold mine effluents may be different from those associated for coal mine effluents. Similarly, some refineries in the United States (e.g., Chevron's Richmond, CA refinery) produce process-affected water that contains selenium and are required to treat it prior to discharge. In this case, treatment solutions must account for the low concentration/high volumes scenario typical of refinery effluents. Finally, coal-burning power plants may

generate a selenium-contaminated leachate from uncovered coal ash landfills (e.g., Reliant Energy's W.A. Parish coal ash disposal area, TX), leachate that may require treatment. In each case, a unique solution needs to be developed to treat the contaminated water.

A number of treatment technologies have been developed to remove selenium from contaminated water. These include physical methods (e.g., ion-exchange, reverse-osmosis), chemical methods (e.g., ferric iron precipitation), and biological methods (e.g., bioreactors/treatment plants, treatment wetlands). All these technologies vary in their characteristics, such as treatment efficiency (i.e., percent removal), achievable final effluent concentrations, volumes of water that can be treated economically, temperature-sensitivity, etc. This variation presents some difficulties to compare these technologies and identify the most appropriate solution for coal mines in Alberta.

This document presents the current state-of-the-art on treatment technologies for reducing selenium levels in water. Its main objectives are to:

- Review scientific literature and obtain expert opinion on available treatment technologies to reduce selenium in water;
- Using similar criteria, evaluate the technical feasibility of each technology;
- Recommend treatment options that might be used to reduce selenium in surface water at Alberta mines.

It is expected that new developments on the horizon will amplify or add to this information, but that the fundamental knowledge presented herein will not change.

2 Selenium chemistry

Understanding the characteristics and reactions of selenium provides a context for the potential use and choice of treatment technologies presented in Section 4. Thus, Se chemistry will be briefly reviewed here.

2.1 Physical Properties

Selenium was first identified as an element in 1817 by Swedish chemists J.J. Berzelius and J.G. Gahn. Its atomic number is 34, mass is 78.96, melting point 271°C, boiling point 685°C, and density 4.26-4.79. Se is in Group VIA of the periodic table between sulfur and tellurium. Its electron distribution is similar to that of sulfur, a fact reflected by the similarities of their chemical properties. Like sulfur, selenium occurs in oxidation states II-, 0, II+, IV+, VI+, although the II+ oxidation state is not known to exist in nature. Se is considered a metalloid because it possesses both metallic properties (e.g., semi-conductor) and non-metallic properties (e.g., elemental Se is dull, without metallic shine).

Se is present in the environment in both inorganic and organic forms. The inorganic forms are elemental Se (Se°), selenite (Se[IV], SeO_3^{2-}), selenate (Se[VI], SeO_4^{2-}), and hydrogen selenide (Se[-II], H_2Se) (See Figure 2). The oxidized forms of Se exist as soluble oxyanions in aqueous environments, with selenate dominant in freshwater and selenite dominant in seawater. Neither of these anions react with cations (e.g., Ca, Mg) under normal ambient conditions, thus remaining soluble in most water bodies. Elemental Se is found in either an amorphous state (an easily identifiable crimson red form, see Figure 1) or in one of three crystalline states. Most stable is the gray, semi-metallic crystalline form which exhibits photoconductive properties and has various industrial uses.

Figure 1. Elemental selenium formed by bacterial reduction of selenate.

Reduced Se species include inorganic forms, such as hydrogen selenide (H_2Se), and organic forms such as volatile methylselenides and nonvolatile organic compounds. Methylated forms are volatile, sparingly soluble and comparatively non-toxic. The Henry's Law constant for dimethyl selenide, the most commonly volatilized species, has been reported as 0.058 (5) and 0.0879 (for both dimethyl selenide and dimethyl diselenide, 6). Most organic non-volatile organoselenides have not been characterized. These species have direct carbon-Se bonds and are biologically active as selenoamino acids and selenoproteins. Two of these compounds are selenocysteine and selenomethionine, which are highly toxic analogs of the sulfur-bearing amino acids cysteine and methionine.

Se is almost exclusively associated with sulfur in endogenic processes (those occurring inside the earth), but differences in melting and boiling points and in redox potentials mean that they follow different paths

in exogenic processes. The similarities in ionic radius (198 pm for Se vs. 184 pm for S) allow for ionic substitution of Se(II-) for sulfur in sulfur minerals. Mineral selenides are usually found in association with sulfur minerals such as chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and galena (PbS), forming seleno-counterparts to these sulfur minerals, such as selenopyrite (SeFeS). Elemental Se can also react directly with reduced sulfur compounds to form insoluble selenosulphides, e.g., Se_2S_3.

Selenates and sulfates have similar colors, ease of crystallization and water solubility, but have different decomposition pathways. While sulfates decompose to give the metal oxide, sulfur dioxide and oxygen, the equivalent mineral selenates typically decompose to give the metal-selenite and oxygen. This results from the greater stability of salts in the selenite-selenate system. Selenides of heavy metals such as mercury, silver, copper and cadmium are highly insoluble, which may explain an association between selenite and decreased heavy metal toxicity.

In coal, Se is one of the most strongly enriched element, being present as an organoselenium compound, in solid solution with pyrite and other sulfides, and as lead selenide (7, 8). It is primarily associated with the organic constituents and micron-sized sulfides and selenides, but is highly variable as a result of the variability of its sources.

Se is used extensively in the production of glass, pigments, rubber, metal alloys, textiles, petroleum, and photoelectric applications. The use of Se-based pesticides has been curtailed largely due to their stability in soils and resultant contamination of food crops, and their toxicity to mammals and birds (2).

2.2 Chemical Properties and Reactions

The many possible oxidation states of Se make for a complex chemistry. Interactions are further complicated by biologically mediated oxidation-reduction reactions. Speciation in soil solution is governed by various physico-chemical factors expressed in terms of pH, dissociation constants, solubility products, and oxidation-reduction potentials (9).

2.2.1 *Oxidation/Reduction and Solubility*

Se speciation is highly influenced by reduction/oxidation (redox) chemistry. This is especially important because Se oxyanions (sel*enite*: Se(IV) and sel*enate*: Se(VI)) are highly soluble, while the reduced forms (elemental selenium: Se^0 and sel*enide*: Se(II-)) are insoluble. It is the solubility of the oxidized forms that allows for their mobility in the environment and their biological uptake. As with sulphur compounds, selenite is quite reactive and is more easily reduced to elemental Se. Most selenite salts are less soluble than the corresponding selenates. The extremely low solubility of ferric selenite $Fe_2(SeO_3)_3$ ($K_s = 2.0 \pm 1.7 \times 10^{-31}$), and of the basic ferric selenite $Fe_2(OH)_4SeO_3$ ($K_s = 10^{-61.7}$), is important to the environmental cycling of selenium, as well as providing a basis for treatment (10).

Figure 2 shows the areas of thermodynamic stability for the Se-H_2O system in relation to redox potential (Eh) and hydrogen ion potential (pH). Typical redox potentials for environmental media are in the following ranges: Surface water (pe 1 to 6); groundwater (pe -1 to 1); wetland sediments (pe -4 to 1).

These distributions assume that equilibrium is established, a condition that is rarely met. Thus, the reduction of selenate to selenite is thermodynamically favoured but this reaction is very slow (days) and is rarely complete. In contrast, selenite is reduced to insoluble forms in a matter of hours at low redox potential (11). In fact, selenate, selenite, and biselenite ($HSeO_3^{2-}$) are commonly found outside of their predicted zones of thermodynamic stability. Both H_2Se and HSe^- also occur but are comparatively uncommon.

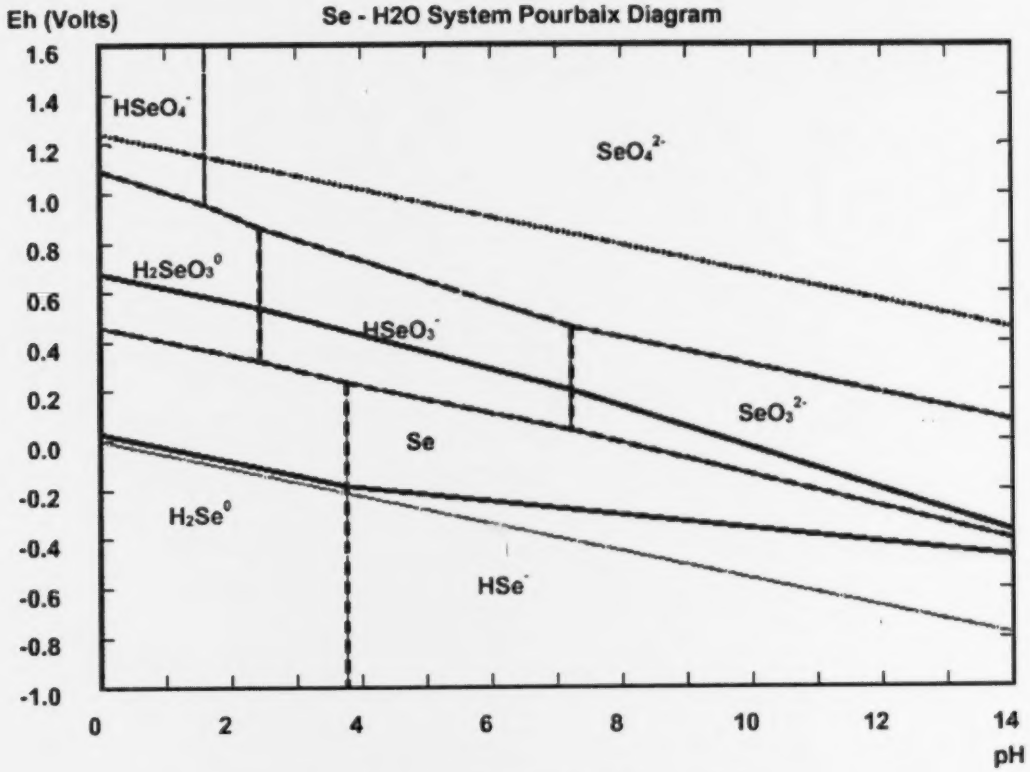

Figure 2. Eh-pH diagram for Se-H_2O system.

The transformation of selenate to selenite, while thermodynamically favoured, occurs slowly because the activation energy for this reaction is very high. ***The feasibility and/or economics of different treatment systems often revolves around this fact.*** Typically, chemically-based treatment processes require an initial reduction of selenate (stable) to selenite (reactive) using strong reductants (e.g., zinc powder). In contrast, microbes catalyze this reduction at ambient conditions, a strength of biologically-based processes.

Calculated reaction equilibria and constants at environmentally-relevant oxidized or moderately reduced conditions indicate that metal-selenite and metal-selenate minerals are too soluble to persist in soils and sediments (12). Under these redox conditions, Se solubility appears to be governed by an adsorption-type mechanism rather than precipitation/dissolution reactions. At low redox potentials, elemental Se or a metal selenide are predicted to limit Se solubility. Since hydrogen selenide (H_2Se) is a highly reactive species, it will be transformed into metal selenides such as FeSe and $FeSe_2$, or ionically substituted into metallic sulfide minerals such as chalcopyrite ($CuFeS_2$) and pyrite (FeS_2). Either elemental Se or these insoluble minerals could act as potential sinks for Se.

Naturally, as redox conditions change, reduced compounds could become sources of soluble selenium. Oxidation of elemental selenium and Se-containing pyrite was credited as a source of increased soluble Se concentrations in Kesterson Reservoir sediment suspensions (13). Similarly, the continued release of selenium in the British Columbia and Wyoming coal fields, and in the Idaho phosphate region, has been shown to arise from the oxidation of Se-containing pyrite (14, 15). The former examples are relevant to the Alberta foothill coal mines, because they likely share common geological origins, including

Cretaceous marine shales, which may have high Se concentrations (16). It suggests that selenium release may persist for decades, as long as the sulphide minerals are exposed to the atmosphere and allowed to weather.

2.2.2 *Methylation and Volatilization*

Dimethyl selenide (DMSe, $(CH_3)_2Se$) and dimethyl diselenide (DMDSe, $(CH3)_2Se_2$) are two volatile species of Se. In natural waters, the production of DMSe is proposed to involve enzymatic and nonenzymatic processes. Methylation is one way for organisms to eliminate excess Se, and aerobic and anaerobic bacteria and fungi capable of doing so have been reported (12). Se volatilization in plants also appears to be a detoxification mechanism and is correlated with tissue Se concentration. Threshold Se concentrations at which volatilization occurs, and rates of volatilization will vary with species for a given water chemistry. DMSe volatilizes rapidly due to its limited water solubility and high vapor pressure. Volatilization rates of Se from soils and plants are also affected by temperature, moisture, time, season, concentration of soluble Se, and microbiological activity. Addition of carbon, alkaline pH values, and oxidation to moderately reduced conditions stimulate biomethylation of Se (12).

Hydrogen selenide (H_2Se) is another volatile species. It may be produced and released in reduced environments, but it oxidizes quickly to elemental Se in the presence of oxygen.

2.2.3 *Other Reactions*

Complexation reactions can also occur with Se, and ion pairs such as $CaSeO_4^{\bullet}$, $CaSeO_3^{\bullet}$ together with the dissociated SeO_4^{2-} and $HSeO_3^{-}$ species are predicted to be thermodynamically dominant. However, unlike sulfates and sulfites, concentrations are rarely high enough to allow such associations in significant quantities.

Selenite adsorbs to surfaces far more than selenate. Sorption can be onto detritus, clays, Fe- and Mn-oxyhydroxides, or onto soils, and each is pH-dependent (12). Like phosphate and sulfate, the association of selenite with Fe- and Mn-oxyhydroxides is very strong and is described as a ligand exchange reaction, whereby –OH groups on the surface of the mineral are replaced (17). There is a treatment process that exploits this reaction for selenium removal.

An interesting abiotic transformation is the reduction of selenate to elemental Se in the presence of Fe(II,III) oxides known as Green Rust (GR). GRs were initially found as intermediate products of the reduction of iron oxides in aqueous systems, but have recently been found as minerals (i.e., compounds forming in a natural environment). Only in the past few years have the environmental occurrences and implications of GRs been considered. The catalyzation of the selenate redox reaction by GR may represent a pathway for Se cycling which had previously been considered to be mediated by microorganisms. The rapid oxidation of green rust has allowed its presence to be overlooked in the past, but recent studies give evidence of its presence in soils, sediments and porewaters. The reduction reaction can be described as follows:

$$HSeO_4^- + 4Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 \cdot 3H_2O \Leftrightarrow HSe^- + 8Fe_3O_4 + 4SO_4^{2-} + 8H^+ + 32H_2O$$

This may occur either through coprecipitation and reduction in GR interlayers, or by adsorption on the GR surface. Myeni et al (18) investigated this transformation and found that green rust catalyzed the reduction of selenate in anoxic conditions with pH>5.0. The degree of reduction varied with pH (greater at higher pH), the nature of the reaction (coprecipitation or adsorption), and the initial concentration of Fe(II). Synthetic green rusts have been developed for corrosion studies by oxidizing $Fe(OH)_2$, incorporating Cl^-, SO_4^{2-}, or CO_3^{2-} ions (19). Our understanding of this mechanism is still in its infancy, but investigation into the remedial possibilities for GR in wetlands is certainly warranted.

3 Source Control

The expected length of time for the release of selenium at the mountain coal mines in west-central Alberta is not known at this time. Thus, it is not known how long selenium levels will remain elevated or if selenium levels will increase over time. At the Alberta mines it is possible that selenium mobilisation due to mining activities or disturbance may be a long-term problem. This is expected to be the case at the Elk Valley River coal mines in Southeastern BC because selenium is associated with sulphide minerals (15), which may oxidize for decades. A similar problem exists at many metal mines, which may leach metals for decades after closure. These mines have developed a number of strategies to minimize or mitigate metal release from waste rock. Time and again, it has been shown that preventative measures are the most cost-effective way to mitigate impacts from contaminants leached from waste rock. These measures include preventing or minimizing sulphide oxidation (submerging sulphide minerals, covering waste rock with air or water impermeable soil covers) or managing the contaminants in place (e.g., using *in-situ* treatment, phytoremediation).

In Idaho, both coal and phosphorus mines contain highly seleniferous shales that represent long-term sources of selenium in the environment. Mining companies in that state have collaborated with the US Forest Service (USFS) and Bureau of Land Management (BLM) to develop Best Management Practices (BMP) that minimize the release of selenium from these materials. For example, shales with high Se are identified during mining and are returned to open pits, where they are covered with 8-10 feet chert (non-seleniferous), then capped with top soil, as a means of minimizing Se release (20). This and other BMP are currently being formalized and collated, and are expected to be available by the time this report is published[1].

Two of the most common preventative methods used to minimize Se release will be discussed briefly, since they form a component of the overall treatment solution at mine closure.

3.1 Submerging Sulphide Minerals

Submerging tailings containing sulphide minerals, or "subaqueous disposal", is practiced at metal mines. The low dissolved oxygen concentrations in the water overlying submerged tailings keeps oxidative rates at a minimum. Furthermore, reducing conditions may develop at depth, near the surface of tailings, thereby halting oxidation altogether.

This approach was extensively studied by metal mining companies. One of the key reports from these studies (21) was that sulphides in tailings either did not release metals, released minor amounts of some metals (e.g., zinc), or release soluble metals (e.g., arsenic) originating from minerals that were oxidized during processing (milling). A companion study that reviewed effects from submerged tailings reported that there are no demonstrable aquatic impacts (22).

Another application of this method is the flooding of underground mines, where metal leaching rates decrease dramatically upon flooding. For instance, zinc concentrations in the Galkeno 900 adit discharge decreased gradually as the underground workings flooded after a concrete plug was installed in the adit (23).

[1] Further information should be available from the USFS, Soda Springs office, or the BLM, Pocatello, ID.

3.2 Soil Covers

In most circumstances, placing engineered soil covers on rock that releases selenium is likely to substantially decrease loadings.

Covers are constructed from natural or man-made materials that retard or divert the movement of water and oxygen into areas containing oxidizing rock[2]. Soil covers can achieve substantial reductions in water flow through piles, but generally do not completely stop sulphide oxidation. For instance, a cover placed over waste rock dumps at the former Rum Jungle Mine reduced sulphide oxidation rates by a factor of 2-3, based on 15 years of monitoring (24). These covers are typically designed by soil engineers, based on material availability, climate, anticipated life, treatment objectives and desired performance (25).

There is a great deal of information available on soil covers, but it will not be reviewed here because it is peripheral to the main focus of this document. Much of the research is published in proceedings from mining conferences, such as those of the International Conference on Acid Rock Drainage (ICARD) or the American Society for Surface Mining and Reclamation (ASSMR). Additional information is available from various research groups (e.g., Unsaturated Soils Group, Dept. Civil Engineering, University of Saskatchewan; The Australian Centre for Mining Environmental Research (http://www.acmer.com.au); consulting firms (e.g., O'Kane Consultants Inc. http://www.okane-consultants.com), etc.

[2] Plastic liners are rarely used because covering large volumes of waste with a liner is usually too expensive.

4 Treatment Systems

Although many different processes have been examined for the removal of selenium from surface waters contaminated by selenium, only a few engineered solutions have been shown to be successful on a commercial scale. In the past, the most widely used approach involved chemical co-precipitation with iron salts at an acidic pH. However, this process is only effective with selenite, and it will not consistently decrease Se concentrations to currently existing discharge criteria. Recent advances in membrane technology and biological processes have brought a new generation of treatment systems. These various systems are reviewed below.

Selenium treatment can be divided into physical, chemical, and biological processes, as shown in Table 1.

Table 1. Types of treatment systems available for selenium.

Physical	Chemical	Biological
Reverse Osmosis	Zinc or iron reduction	Volatilization
Nanofiltration	Iron precipitation	"In-situ" treatment
Ion Exchange	Cementation	Bioreactor
Deep Injection/ Evaporation		"Passive system", i.e., Biopass, Reactive Wall
		Treatment wetland

Reverse osmosis (RO), nanofiltration, and ion exchange remove selenium from an effluent by concentrating it into brines or wash solutions. The resulting concentrates must be disposed safely, either by deep-injection, evaporating the solutions, or other methods.

Chemical methods rely on the reactivity of selenite (Se(IV)), whether with iron or other reagent. Typically, a pre-treatment is required to chemically reduce Se(VI) to Se(IV), using (most commonly) elemental iron or zinc. Such a reduction of Se(VI) is not normally required for biological treatment, but other forms of pre-treatment may be required, such as removal of nitrate[3]. These different pre- and post-treatment steps add to the complexity of the system (its design, operation, etc) and they must be included in any calculation of treatment cost.

Technologies are commonly evaluated by comparing the cost for treating 1,000 gallons of mine water. This cost is either explicitly expressed as an operating cost, or is implied as an amortized capital cost + operating cost for a defined period (e.g., ten years).

When comparing different treatment systems, two factors must be kept in mind. First, the system eventually adopted may make sense for that mine or industry, but not elsewhere. Thus, at Lac Mineral's (now Barrick) Richmond Hill Mine, iron reduction followed by iron co-precipitation was selected partly because tanks used for the carbon-in-pulp gold extraction could be marshaled to this task. Similarly, the Biopass system developed at Homestake's (now Barrick) Santa Fe Mine made sense because the

[3] Bacteria that utilize nitrate to oxidize organic matter derive more energy than those that use selenate or selenite. This confers an advantage to them and allows them to outcompete selenate-reducing bacteria. In practice, nitrate will be removed before selenium in any biological treatment system.

drawdown water from the spent heap was to be released for a limited time, flows were limited, other contaminants (e.g., nitrate, mercury) were also treated in the system, and because lined, open ponds were available for this system. Economics greatly favoured these systems because these facilities were available, thereby reducing capital costs.

The only way to compare "apples with apples" is to evaluate side-by-side different technologies that treat the same water. Such an evaluation was conducted recently by the U.S. EPA, and its results will be reviewed.

A second factor to consider is the gap between technology development and adoption. Thus, nanofiltration is a very promising technology, but no one is willing to be the "test case" in the industry. Consequently, this technology sits on the shelf, waiting for someone to give it a try. However, this situation is changing in the U.S.A. because of the stringent regulatory requirements to treat selenium to very low concentrations.

4.1 Physical

Physical methods used for selenium removal include membrane filtration and ion exchange (electrostatic interactions) methods. Membrane filtration does not discriminate between selenate and selenite, but ion exchange does, being only effective on the latter. Thus, a pre-reduction step is required for treatment of selenate-containing water by ion exchange.

Adsorption onto activated carbon has not proven effective for selenium removal, at least in achieving the low concentrations (< 5 ug/L).

Generally, treatment systems based on these processes are expensive, due to the requirement for pre-treatment steps and post-treatment disposal of concentrated reject brines, as discussed below. This has limited their application at mine sites.

4.1.1 *Membrane Filtration*

Reverse osmosis (RO) and nanofiltration are two membrane filtration methods for treating contaminated water. RO is a widely used and tested technology, whereas nanofiltration is relatively new. Both technologies use a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. The membrane for nanofiltration is different from that used in RO, in being charged and having a hydrophobic reject layer, thereby selectively rejecting divalent salts while retaining monovalent salts. Most RO technology uses a process known as crossflow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected species away from the membrane.

Membrane filtration requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases. The pressure can reach 1,000 psi, and this requirement constitutes a high proportion of the operating cost. In this respect, nanofiltration is attractive because it operates at lower pressures, and therefore costs less to operate.

Their ability to meet acceptable discharge criteria depends on the characteristics of the mine water to be treated. It is generally agreed that complex or hard waters cannot be treated to below 10 ppb (26). Successful treatment requires a water softening plant to pre-treat mine water. In any event, this would normally be required to prevent excessive membrane fouling, as described below.

There are problems inherently associated with these technologies. Fundamentally, treatment is extended until constituents of concern (e.g., Se) reach the desired final concentrations. As solutes are being concentrated, some salts initially present at high concentrations may crystallize, thereby impairing function or damaging membranes. This is particularly true for hard waters containing high calcium and magnesium concentrations. In general, membrane life is expected to be 2-3 years, depending on the Total Dissolved Solids (TDS) of the water being treated.

In addition, the concentrated brine containing the rejected contaminant(s) must be dealt with safely and cost-effectively. This may require an evaporation facility to dispose of the brine, deep-injection, or some other method. These options can be expensive, depending on the volume of brine to be disposed.

Treatment costs are high, which has limited application of this technology at mines. Depending on necessary pre- and post-treatment requirements, operating costs can range from USD$4.7-71/1,000 gallon, with a median around USD$10-15/1,000 gallon. Capital costs can exceed USD$1 million for the RO unit alone, depending on volumes being treated.

At Lac Mineral's (now Barrick) Richmond Hill Mine, reverse osmosis was selected to treat mine water that is incompletely treated by iron reduction and precipitation (described below). The latter decreases Se concentrations from over 100 ppb to 12-22 ppb, whereas RO decreases it further to approximately 2 ppb. The RO unit is operated at 250 psi and up, which contributes substantially to the operating cost. Flows of 200 gpm are fed to the RO unit, and it produces a permeate at 100 gpm and a reject stream at 100 gpm. This brine, which is a Se concentrate, is cycled back to the iron treatment circuit. Given that selenium is produced from 52 acres (21 hectares) of leach pads, water treatment is expected to be required for at least 50 years.

A filtration pre-treatment is necessary to remove TSS. In addition, the operator is currently evaluating the need to remove calcium in a softening plant. Calcium concentrations in the feed have gradually increased to the present 450 ppm, causing gypsum to be deposited on membranes as salts become concentrated. The cost of this additional softening plant is compared against that of the shortened membrane life, which is presently replaced every 1-2 years at USD$30,000, instead of the normal 3 years.

During winter operation, water is heated to 15 °C to prevent the cold-induced salt crystallization[4] on membranes. The heating cost is approximately $USD5,500/week, and depends on the weather[5] and propane costs.

The capital costs include purchase of a used RO unit at USD$750,000 (a new unit with the same capacity is approximately $1.2 million) and a multimedia pre-filtration unit at $200,000. Overall monthly operating costs are $50,000, or $10/1,000 gallon when the RO unit operates without trouble. The above issues are presently increasing treatment costs to $18/1,000 gallon. Some of these problems stem from changing water chemistry, some are caused by algal growth.

Nanofiltration is potentially less expensive than RO, due to its more selective nature and the lower pressures under which it operates. There are no examples of mines currently using this technology, although Newmont has evaluated its use at the closing Yanacocha Mine, in Peru to remove sulphate and thallium.

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[4] Concentrated salts are less soluble in the cold.

[5] South Dakota winters are comparable to Alberta winters.

The same issues of membrane fouling must be considered: pre-treatment for high TDS, addition of anti-scalants, anti-bacterial agents and Total Suspended Solids (TSS) removal may be necessary. These can add 10-20% to the operating cost of treatment.

Capital costs for a single-stage filtration unit are quoted at USD$2,000/gpm feed: a plant treating 500 gpm would cost $1 million (27).Additional pre-treatment may be 50% of the treatment plant cost, ranging from $300 - 1,000/gpm feed. Operating costs are quoted at approximately $0.50-0.60/1,000 gallons for a nanofiltration unit, with an additional $0.10-0.15/1,000 gallons for additional pre-treatment. This is much lower than operating costs for RO, but there are no operating nanofiltration units from which these costs could be verified. Additional maintenance costs include changing membranes every 2-3 years.

Development time is relatively short. Laboratory scoping studies can last two weeks, followed by a pilot campaign lasting one month, including mobilization and demobilization. System design can take one week, and ordering can take 20-24 weeks. Thus, a plant can be operational within half a year, assuming a fairly simple design. Additional delays will come from the requirement for, design and construction of pre- and post-treatment units.

4.1.2 *Ion Exchange*

Ion exchange is a reversible reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Efforts to use zeolites for selenium removal have met with limited success. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

Selenium removal is accomplished by using a strong base anion ion exchange resin. Se(VI) is extracted much more effectively than Se(IV). The extraction of Se(VI) is decreased by sulphate. Tailored resins show good selectivity for selenium in the presence of sulphate but only laboratory studies have been performed. Further laboratory studies (on mine waters) are required.

Once the capacity of the resin becomes exhausted, it must be regenerated with a strong acidic solution. As with RO and nanofiltration, the disposal of this solution adds to the overall cost of this technology.

Liquid ion exchange has been investigated on a pilot scale for treating gold heap leach solution effluents. The results were encouraging but the technology has been documented at only one site. Further laboratory and pilot test work need to be conducted.

4.2 Chemical

Several chemically-based treatment processes have been investigated, but only iron co-precipitation has met with success on a commercial scale. Precipitation with activated alumina has not met with success, though it has been tested extensively. Precipitation on lanthanum oxides looks promising, but has not yet been tried beyond the laboratory.

4.2.1 *Iron coprecipitation*

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface is an USEPA-approved technology for treating selenium-bearing waters. For the coprecipitation to occur, ferric ion (Fe^{+3}) must be present in the water. The chemical reaction for ferrihydrite precipitation of selenium is:

$$Se^{+4} + FeCl_3 + 4H_2O \rightarrow Fe(OH)_3 \bullet Se^{+4} + 8H^+$$

Adsorption on ferrihydrite has been investigated by several researchers. Se(IV) is effectively removed at pH < 8. This technology is not very effective for Se(VI) except at high Fe/Se weight ratios and relatively low pH levels. Reduction of Se(VI) prior to adsorption is required for effective removal. The presence of other aqueous species may have a detrimental influence on the removal of Se(IV) and Se(VI).

In a review of this technology, Tidwell and co-workers (28) indicated that:

- Se(IV) is adsorbed much more effectively than Se(VI);
- Se(IV) adsorption is a function of type of oxyhydroxide present (amorphous ferrihydrite is best, crystalline FeOOH is considerably less effective);
- The initial concentration of Se(IV) in solution is very important (the higher the Se(IV) concentration the more effective the adsorption);
- The best pH for effective Se(IV) adsorption is 4-6 (85-90% removal), adsorption decreases slowly until about 7 (80-85% removal), then decreases drastically to about (20-40% removal)

In early studies on selenium treatment, Merrill and co-workers (29) reported an optimum pH of 6.5 for Se(IV) removal and that the optimum iron dosage was 14 mg/L for a water initially containing 40-60 µg Se/L. The effluent selenium concentration resulting from the treatment of 33 gpm in a continuous pilot facility was < 10 µg/L. The process treatment created 2.1-3.1 kg sludge/kg iron added. The estimated cost of processing 26 million gallons/day (for arsenic, heavy metals and selenium removal) would be USD$ 0.50/1000 gallons. This estimate, which seems very optimistic, is based on a flowsheet consisting of ferric chloride addition to form ferrihydrite, rapid mixing, polymer addition for agglomeration, clarification, sludge thickening and dewatering, and disposal of dewatered sludge in a municipal landfill.

The effect of other anions on the adsorption of selenium has been investigated (30). Certain anions were found to preferentially adsorb onto ferric oxyhydroxide. The order of adsorption at pH 7 was found to be phosphate > silicate = As(V) > bicarbonate/carbonate > Se(IV) > oxalate > fluoride = Se(VI) > sulphate. The order of adsorption at the lower pH used in treatment plants may be different.

The long term aging stability of adsorbed/co-precipitated selenium remains to be demonstrated. Adsorbed Se may be released when amorphous iron oxide crystallizes to the more thermodynamically stable phases of goethite (FeOOH) or hematite (Fe_2O_3).

At Lac Mineral's Richmond Hill Mine, a selenium treatment system was developed in 1994, based on a process using elemental iron to reduce selenate to selenite, followed by ferric sulphate precipitation at pH 4.5, with a copper sulphate catalyst. The resulting slurry is sent to a thickener to produce a peanut-butter-like sludge that is stored in a sludge pond.

The treatment process needed three years to be optimized. Even so, the best that could be achieved is effluent Se concentrations of 12-22 ppb, which is unacceptable for direct discharge to the environment. The treatment system is now used in conjunction with an RO treatment, which together produces an acceptable effluent.

A treatment plant was developed at FMC's (now Meridian) Dry Valley Mine for selenium removal (31). The process used zinc powder as a reductant, converting all the selenium to selenite, followed by iron salt precipitation at acidic pH. A similar plant was designed at a Homestake mine, where (elemental) iron powder and ferrous sulphate were used as reductants and ferric chloride was used to form ferric

hydroxide, which co-precipitates selenite. Again, the reaction was carried out at ~pH 4.5 and requires tight pH control (+/- 0.2 pH units).

Although capital and operating costs could not be found for both operations, their design and operation is comparable to the treatment plant for molybdenum removal at Noranda's former Brenda Mine. That treatment plant operates under very similar conditions and removes molybdenum through the same process (Figure 3), although it has been rated at 2,000-4,000 gpm. It is designed to operate for over 100 years, and reportedly costed over CDN$10 million when it was built in 1998 (32).

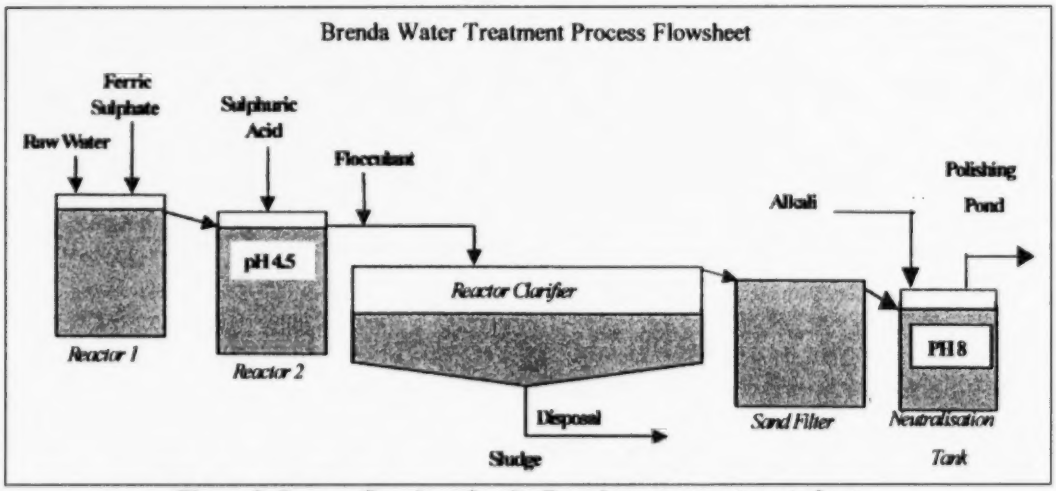

Figure 3. Process flowsheet for the Brenda water treatment plant.

Another chemical process, called catalyzed cementation has been developed by Dr. Larry Tidwell, Montana State University, to remove arsenic, metals and metalloids such as thallium and selenium from water. The term catalyzed cementation describes the process's ability to remove contaminants from solution by cementation (adsorption) onto the iron surface. Catalyzed cementation is expected to treat and remove selenium from solution regardless of its valence state (+6 or +4). To optimize the cementation process, proprietary catalysts are added to increase the removal efficiency of the process[6]. Laboratory tests have shown that selenium concentrations are decreased to below 50 ppb.

This process was tested in a US EPA-sponsored demonstration project at Kennecott Utah Copper Corporation's (KUCC) Garfield Wetlands-Kessler Springs site (33). This demonstration project was established to compare three different technologies side-by-side, thereby collecting comparable performance and cost information.. The site provides water with uniformly high selenium concentrations of 1,600 ppb Se, mostly as Se(VI).

During the test, flows were maintained at 1 gpm. In this process mine water receives iron powder, a proprietary catalyst, and its pH is carefully adjusted to allow for selenate reduction. The iron is recovered for re-use, the solution is pH-adjusted again, another reagent is added, and the cementation reaction is carried out. The suspended solids are thickened and the supernatant is discharged. The entire process is shown in Figure 4.

[6] Terry Mudder indicates that small amounts of copper aid in the adsorption of selenium onto ferrihydrite. This, or another metal, may be the proprietary catalyst.

The catalyzed cementation process could not at first consistently meet the target of 50 ppb Se in the pilot test. However, modification of treatment conditions produced a more acceptable effluent (Figure 5 and Table 2). Additional investigations in the laboratory further improved the treatment process, producing an effluent with selenium concentrations below 5 ppb.

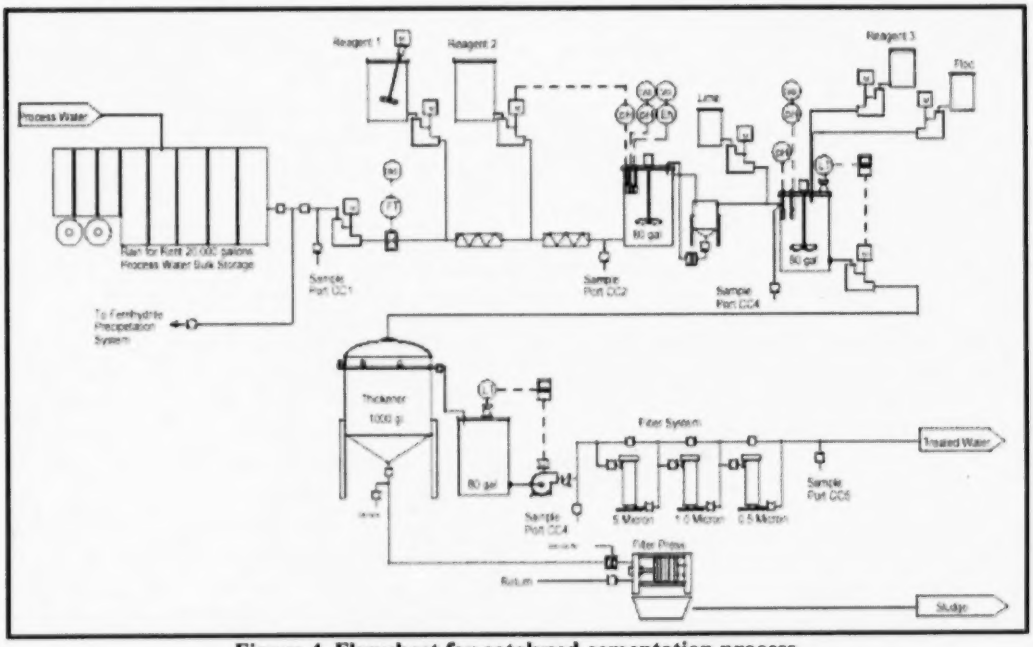

Figure 4. Flowsheet for catalyzed cementation process.

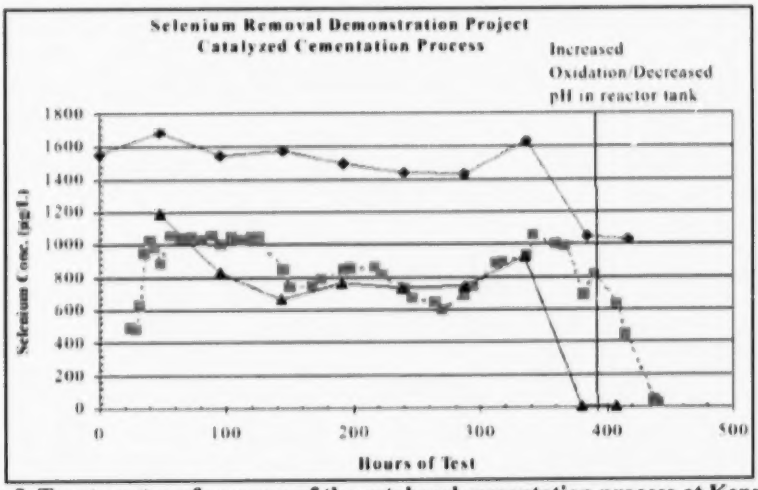

Figure 5. Treatment performance of the catalyzed cementation process at Kennecott.

Table 2. Mean effluent Se concentrations from catalyzed cementation pilot plant.

Treatment Condition	Mean Selenium Effluent Concentration (µg/L) ± Standard Deviation (n = sample size)	Minimum Selenium Effluent Concentration (µg/L)
Catalyzed Cementation	834 µg/L ± 204 (n = 42)	193 µg/L
Catalyzed Cementation with Increased Oxidation/Decreased pH in the reactor tank	35 µg/L (n = 2)	26 µg/L
Additional Testing of Catalyzed Cementation at MSE	3 µg/L 1 ± 4.4 (n = 5)	<1 µg/L

In many respects, catalyzed cementation is very similar to the above conventional iron precipitation technologies. For this reason, the cost comparison with a biological selenium removal technology is instructive. The capital costs for a treatment plant rated at 300 gpm, utilizing some tanks available on site, is calculated to be $1,083,285. Annual operating costs are calculated to be $1,165,358, of which a substantial proportion is accounted by the proprietary catalyst. The treatment cost, amortized over ten years, is calculated to be USD$8.17/1,000 gallons. As will be shown below, this is substantially more than that for biological treatment.

Another iron-based process has been developed at the University of Idaho (34). The process has been piloted and licensed to a company (Bluewater Technologies). Although treatment times are very rapid (10 minutes for low TDS water), final selenium concentrations are still remain higher than acceptable, at a reported 47 ppb. While promising, this technology still requires more development time before it can be evaluated properly for commercial application.

4.3 Biological

Treatment by biologically-based processes relies on the activity of a small group of bacteria that reduce selenate to selenite, then to elemental selenium (Figure 6 and Figure 7). Typically, these bacteria are found in anaerobic sediments, where they use selenium anions to oxidize organic matter. Different bacterial species will form either the red amorphous or the gray metallic form[7]. This may be important since these mineral forms may have different stabilities or susceptibility to oxidation.

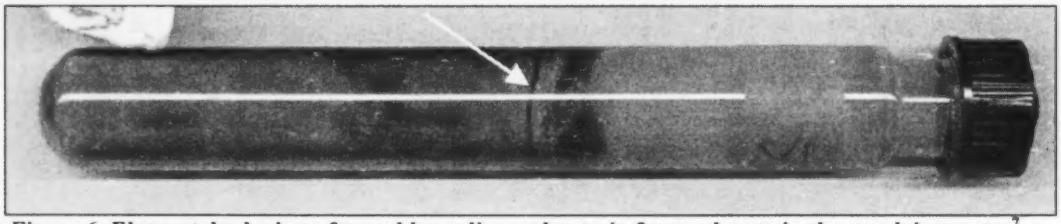

Figure 6. Elemental selenium, formed by sediment bacteria from selenate in the overlying water[7].

[7] André Sobolewski, Microbial Technologies, Inc. Unpublished observation..

Many factors affect their activity, including dissolved oxygen and nitrate concentrations (both are antagonists), temperature, pH, etc. Although it may be beneficial to identify the bacterial species used in a treatment process, this is not always necessary, since it is usually sufficient to identify the conditions that favour maximum activity.

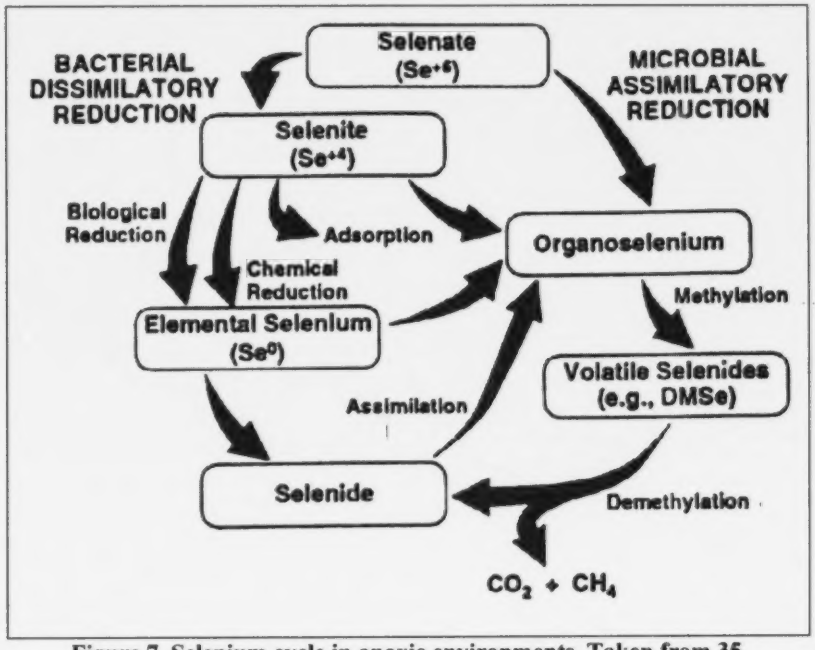

Figure 7. Selenium cycle in anoxic environments. Taken from 35.

The key to successful treatment system design lies in matching bacterial activity (i.e., selenium reduction rate) to the selenium loading rate for a given wastewater stream. This depends principally on the achievable bacterial biomass (more bacteria = higher activity), the supply of nutrients, and temperature.

4.3.1 *Selenium Volatilization*

Frankenberger and Karlson (36) attempted the remediation of sediments from both the Peck and the Kesterson ponds in the West San Joaquin Valley in California. The sediments were amended to stimulate bacterial volatilization of selenium. The Peck pond was bioremediated from a mean of 11.4 mg Se/kg sediment to the goal of 4 mg in 2.6 years. The Kesterson pond was not remediated to the 4 mg goal from 47.8 mg after 8 years, using the same techniques. The results can be explained by examining the distribution of selenium species in these sediments. For Peck the Se distribution was 6.6% Se(VI), 67.6% Se(IV), 18.4% Se(0), 7.3% Se(II-). For Kesterson, it was 5.2% Se(VI), 9.1% Se(IV), 58.0% Se(0), 27.7% Se(II-). Thus, the difference in Se(0) and Se(II-) distributions (25.7% vs. 86%) would suggest that most of the Se in Kesterson sediments was unavailable to microbial volatilization.

4.3.2 *Bioreactors*

Bioreactors are engineered structures that hold selected microbes for wastewater treatment. There are two different types of systems: active systems, essentially conventional treatment plants, in which operational parameters (pH, oxygen concentration, retention time, etc) are tightly controlled, and

passive systems, in which operator intervention is minimal. Both types of bioreactors have been designed for Se removal, as described below.

4.3.2.1 Active Systems

The efforts of the early 1990's to develop bioreactors for treatment of Se in agricultural drainage were reviewed (37). These reactors were mostly small laboratory-scale systems based on anaerobic bacteria that reduce Se oxyanions to elemental Se via the reactions:

$$\text{Se (IV+VI)} + \text{organic carbon} \rightarrow \text{Se (IV)} \rightarrow \text{Se (0)}$$

One of the systems was based on the known selenate reducer *Thauera selenatis*, originally isolated from agricultural drainage (38), whereas the others were seeded with undefined cultures. The reactors utilized either acetate or methanol as carbon sources (methanol being cheaper), and ammonium sulfate as a supplementary nitrogen source. Most of this organic carbon was consumed by bacteria respiring on nitrate (which is abundant in agricultural drainage), outcompeting the selenium-reducing bacteria.

Several reactor configurations were tested, including upflow anaerobic sludge blanket reactors (UASBR), fluidized bed reactors, sequential batch reactors, packed-bed reactors, and slow sand filters (SSF). The latter were found necessary under most configurations because they retained elemental selenium released by treatment bioreactors. Without the SSF, Se concentrations in reactor effluents were typically 30-60 µg/L, whereas they reached 15-30 µg/L with the SSF. These removal rates were achieved with retention times in the order of 10-30 hours. The removal rates were temperature-sensitive.

A common problem identified in most reactors was the formation of calcium carbonate and the potential for plugging. This results directly from the high calcium concentrations present in agricultural drainage and the production of bicarbonate during anaerobic bacteria respiration on nitrate or selenate. Although this makes these treatment systems inherently problematic, it was anticipated that these problems would be addressed during planned pilot tests.

The UASBR pilot plant campaign conducted over a two-year period identified a number of problems. The development of stable biomass took approximately 6 months. This biomass remained stable thereafter, despite variability in sludge volumes retained in the bioreactor. Approximately 90% of Se was removed during the campaign, with influent Se concentrations of 500 µg/L being reduced to 50 µg/L in the discharge. However, this level of treatment was not consistently attained, as effluent Se concentrations occasionally rose over 200 µg/L. This was due to the temperature-sensitivity of the process, as removal rates reached 88% at 15°C, but declined to 35% at 7°C. A partial solution was to insulate reactor tanks for the full-scale treatment system.

Costs were estimated for a full-scale treatment system based on the results from the pilot plant campaign. Operating costs were driven by the relatively high methanol consumption rate, being estimated at USD$1.00-1.30/1,000 gal. The total estimated costs, based on the pilot plant campaign, were USD$1.23-1.48/1,000 gal for a 10 Mgal/day plant, amortized over 20 years. Of course, these costs were derived from the treatment of agricultural drainage and are expected to be different for other types of water.

A number of treatment plants have been constructed and operated at mine sites in the past five years.

At Goldcorp's former Wharf Resources Mine, in Leads, SD, a biological treatment plant has been operated for two years. Mine water containing approximately 30 ppm nitrate (NO_3^-),15 ppb Se (as Se(VI)), and 70 ppb arsenic is collected in a French drain underlying barren rock. Flows are seasonal,

ranging from 40-300 gallons per minute (gpm). All these contaminants are removed during treatment, with NO_3^- decreasing to <1 ppm, Se to < 5 ppb, and As to < 1 ppb.

The plant is operated year-round, with no water heating (except to keep pipes from freezing). Water temperatures range from 1.5-4.0 °C during the winter, to 15 °C during the summer. The rate of bacterial activity decreases somewhat during winter operation, which is compensated with the addition of more nutrient. Problems develop when excessive nutrients are added, as the oxidation-reduction potential decreases to very low levels, causing nitrate to be reduced to ammonia. Otherwise, the system requires little maintenance, and has no scaling or odour (from hydrogen sulphide) problems, though it is checked regularly for sliming or other potential issues.

The overall capital cost for the treatment plant was somewhat under USD$1 million, and annual operating costs are USD$40-60,000. The plant made some use of tanks existing on the property, as well as constructing new tanks. The biggest capital cost item was the purchase of activated carbon as support matrix for the bacteria. A total of 800,000 lbs (362 metric tons) of activated carbon was purchased at USD$0.37/lb.

The system was first tested in the laboratory on a bench-scale, followed by a pilot campaign (Summer 2001) that lasted one month. Design, procurement and construction followed through Fall and Winter 2001/2002. The plant was operational in March 2002. The bacterial inoculum was grown in 3-4 weeks, and does not constitute a significant time constrain.

Overall, this treatment plant functions very well, though contaminant loadings are fairly light.

At the former Zortman-Landusky gold mine, in Montana, the acidic water collected from leach pads is treated biologically before discharge by land application. The neutralized influent to the treatment plant contains approximately 200 ppm NO_3^-, 500-700 ppb Se (as Se(VI)), and 300-400 ppb Total cyanide. The effluent contains <10 ppm NO_3^-, 100 ppb Se, and 200 Total cyanide. While this water does not meet state discharge criteria, it is sufficiently treated to allow for its disposal by land application.

The treatment plant consists of 3 x 250,000 gallon insulated (outdoor) tanks filled with activated carbon. It has treated flows of 75-300 gpm year-round for the past two years. Water temperatures vary seasonally, from approximately 1-15 °C, without affecting treatment performance.

The capital cost for the treatment plant was USD$3 million, for which the highest cost item is the activated carbon (39). Operating costs are somewhat less than USD$250,000/year, and are broken down as follows (Table 3).

Table 3. Operating costs for Zortman-Landusky treatment plant.

Item	Annual Cost
Bacterial nutrients	$100,000
Labour	$43,000
Reagent (lime, etc)	$35,000
Maintenance	$25,000
Power	$15,000
Laboratory analysis	$14,000
Filtration	$10,000
Total	$240,000

A biological treatment system, comparable to the above systems, was tested at Kennecott Utah Copper Corporation's (KUCC) Garfield Wetlands-Kessler Springs site (33). The site provides water with uniformly high selenium concentrations of 1,600 ppb Se, mostly as Se(VI).

The treatment system comprises a series of tanks (total 500 gallon) that contain activated carbon seeded with selected bacteria. The tanks are fed groundwater (temperature = 13 °C) at a rate of 1 gpm and a nutrient solution. The discharge flows through a slow sand filter to remove elemental selenium produced in the tanks. Treatment performance was excellent at all times (Table 4 and Figure 8). Selenium removal was complete, even with a 5.5 hours retention time.

Table 4. Mean effluent Se concentrations from biological treatment pilot plant.

Residence Time	Mean Selenium Effluent Concentration (µg/L) ±Standard Deviation (n = sample size)	Minimum Selenium Effluent Concentration (µg/L)
12 hrs (Series 1)	8.8 µg/L ±10.2 (n = 17)	<2 µg/L
11 hr (Series 2)	4.9 µg/ L ±4.9 (n = 16)	<2 µg/L
8 hr (Series 3)	<2 µg/L ±2.6 (n = 12)	<2 µg/L
5.5 hr (Series 2)	<2 µg/L ±2.1 (n = 26)	<2 µg/L

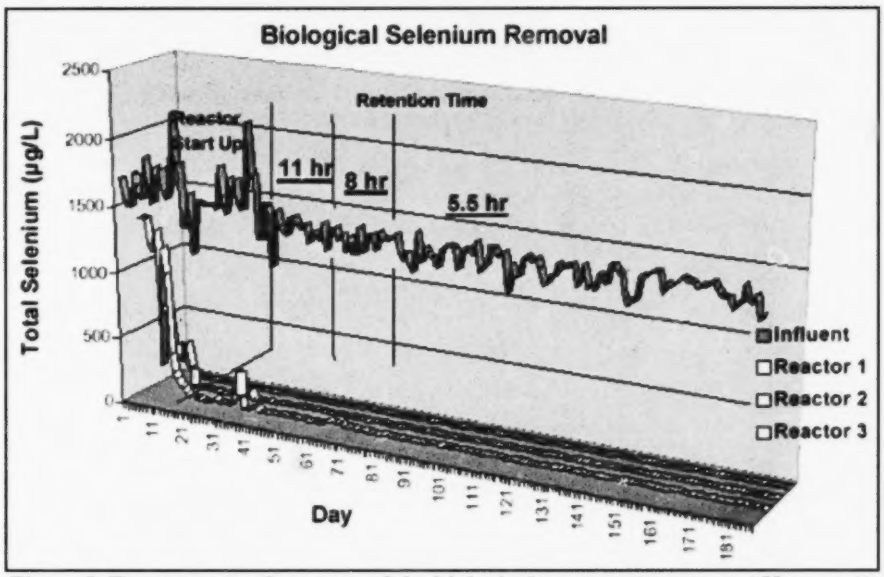

Figure 8. Treatment performance of the biological treatment process at Kennecott.

An economic analysis was carried out to calculate the cost of a full-scale treatment plant receiving 300 gpm of the above groundwater that contains 1,600 ppb selenium (mostly as selenate). The capital costs for such a treatment plant, utilizing some tanks available on site, is calculated to be $603,999. As with the above systems, the bulk of this cost comes from the activated carbon. Annual operating costs are calculated to be $135,029. The treatment cost, amortized over ten years, is calculated to be

USD$1.32/1,000 gallons, a fraction of the catalyzed cementation treatment process. This cost is roughly in line with the costs for the above biological treatment plants.

4.3.2.2 In-Situ Remediation

In-situ remediation involves the treatment of selenium in groundwater through stimulation of bacterial activity. In one typical application, aquifer sediments are sampled for the presence of selenium-reducing bacteria (See Section 4.3) and, if present, they are stimulated by addition of nutrient solutions (40). The reduction of selenate and selenite produces elemental selenium, which is retained in the subsurface.

This approach is been carried out in full-scale at Homestake Mining Co.'s Grants New Mexico Reclamation Project (41). Se present in a groundwater plume at 50-100 µg/L is being decreased through the action of bacteria to <5 µg/L. This process is very cost-effective, at less than USD$1.00/1,000 gallons, due to low capital costs. However, this approach may not be applicable everywhere, due to different aquifer characteristics. Moreover, the potential remobilization of elemental selenium retained in the subsurface has not been conclusively ruled out.

4.3.2.3 Passive System

The Biopass system was developed in the early 1990's for passive treatment of drainage from a reclaimed cyanide heap leach facility at Homestake Mining Company's Santa Fe Mine, in Mineral County, Nevada (42). This system relies on the flow of mine water through decaying organic matter (Figure 9). The system is designed to treat weak acid dissociable (WAD) cyanide (CN), nitrate (NO_3), mercury (Hg), and selenium (Se).

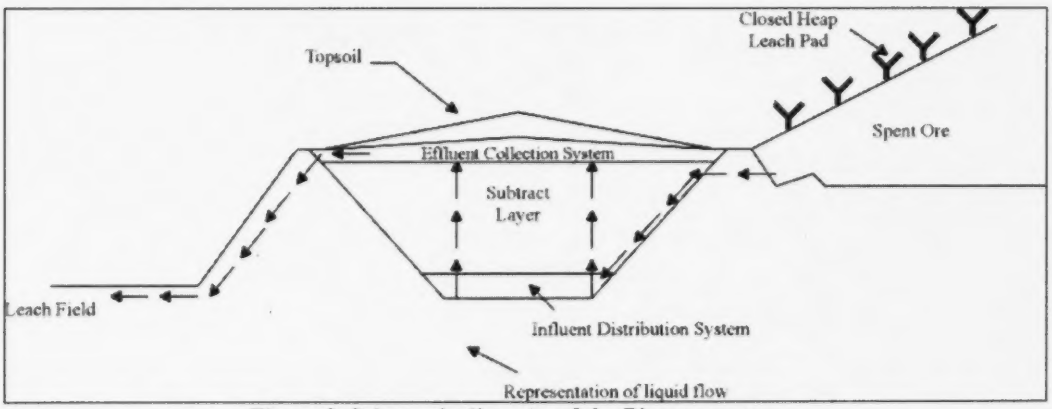

Figure 9. Schematic diagram of the Biopass system.

The Biopass system was constructed in an emptied double geomembrane lined solution pond and consisted of, from the bottom upward: a seepage collection (influent) layer comprised of gravel and perforated pipe, a substrate layer comprised of spent ore gravel and composted cow manure mixture, an effluent collection layer comprised of gravel and perforated pipe, a geotextile cushion, a geomembrane liner, and a vegetative soil cover. Treated solution flows by gravity through a buried pipeline from the effluent layer to a leach field where it is aerobically treated. Anaerobic bacteria in the substrate layer reduce selenium oxyanions to insoluble elemental selenium and form insoluble mercury sulfides. They also remove sulfate from the effluent. Other microorganisms biodegrade cyanide and remove nitrate from the water.

The Biopass system is designed to be sealed and operated passively. As a consequence, living organisms are not exposed to the fixed selenium and metals. However, these contaminants must be prevented from re-oxidizing in the future, or the system must be sealed off to prevent the discharge of re-oxidized contaminants.

Careful attention must be paid to two key considerations in the system design:

- Sizing of organic substrate mass and treatment retention times.
- Design and placement of the substrate layer to minimize consolidation and maintain permeability.

The required mass of organic matter is calculated on the basis of the anticipated sulfate load requiring treatment. A predicted sulfate load is calculated using the average annual flow rates, summed over a 20 year period with two 100 year 24-hour storm events, and an average sulfate concentration of 2,000 mg/L. The mass of organic substrate is determined assuming a conservative ratio of volatile suspended solids that will be consumed per pound of sulfate. Results to date indicate that every contaminant of concern is removed sufficiently for the effluent to meet mandated discharge criteria.

No cost information is available on this treatment system.

The Biopass system is a particular design of a general class of passive treatment systems that has been developed in the past 5-10 years. Such systems that have been used at other mine sites, though they were not designed to treat selenium-contaminated waters (See examples in Figure 10).

In general, they are very compact systems, a distinct benefit in certain settings. The majority of designs rely on the organic matter placed in them to feed the bacteria that provide treatment. Typical materials include alfalfa, manure, mushroom compost, sawdust, straw, etc. The benefit of this design is that organic matter is usually abundant and inexpensive. Its decomposition produces the anaerobic environment required by SRB, nitrate- and selenium-reducers.

The main drawback of this approach is that this material often offers poor or deteriorating system hydraulic, due to gradual decomposition, compaction, sliming, accumulated metals, etc. For that reason, most current designs are best suited for modest flows. Potentially, they represent a "walk-away" scenario, or an inexpensive solution for abandoned mines, specially since some of them have been shown to operate at low temperature.

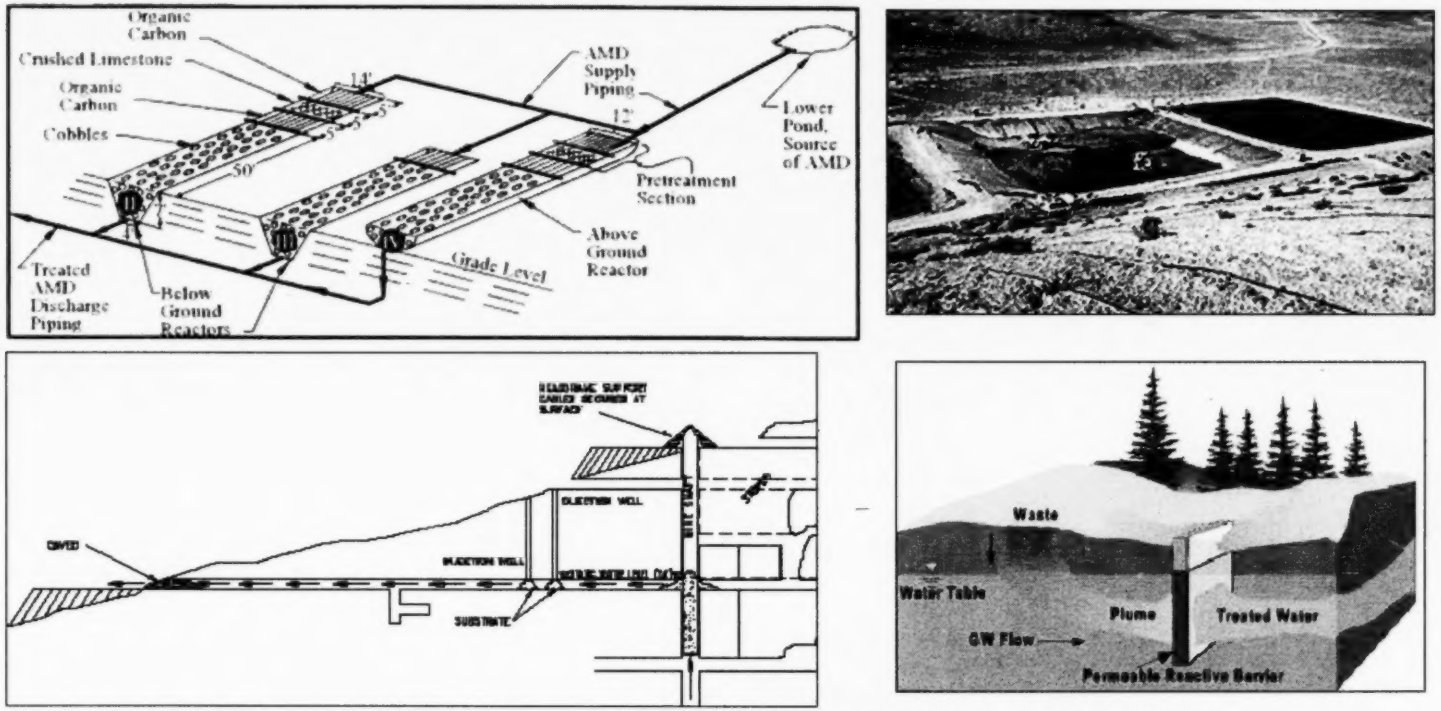

Figure 10. Examples of different bioreactors. Top: aboveground reactors; bottom: underground reactors.

4.3.3 *Treatment Wetlands*

ChevronTexaco's (Chevron's) Richmond, CA refinery, one of the largest on the West Coast, produces a contaminated effluent when selenium is stripped from crude oil during the refining process. The resulting wastewater passes through an oil-water separator, oxidation ponds, and ultimately through restored wetlands which remove Se (43). The 3x30-acre cells (called "passes") wetland system (Figure 11) receives flows of 1,000 gallons per minute (gpm) containing 10-30 ppb (predominantly selenite), a mass loading of 156 ± 13 g/day. Se concentrations are reduced by 60-70% at the outlet on Pass 1 and attain < 5 ppb dissolved Se at the outlet of the wetland complex.

Most of the dissolved Se is retained in the wetland sediments, where it has built up to concentrations of 3-8 mg/dry kg (44). A significant portion of the Se, estimated at 10-30%, is transformed to volatile selenides, which are lost from the system (44). Rates of volatilization in the wetland vary over two orders of magnitude and are a function of time of year and plant coverage (Table 5).

Table 5. Volatilization rates in Chevron's treatment wetlands.

Site	Volatilization Rate μg Se/m²/day
Vegetated - Rabbitfoot grass	190 ± 150
Vegetated - Cattails	180 ± 100
Vegetated – Saltmarsh bulrush	150 ± 40
Vegetated – Saltgrass	80 ± 40
Vegetated – Brass buttons	60 ± 30
Unvegetated – Inlet channel	170 ± 30
Unvegetated – Fungal mat	110 ± 60
Unvegetated – Algal puddle	50 ± 20
Unvegetated – Uncovered sediments	20 ± 10

The wetland has attracted considerable attention because of its abundance of bird life. The marsh is home to black-necked stilts, Canada geese, Savannah sparrows, endangered California clapper rails, as well as grey foxes, raccoons, skunks, muskrats, mice and moles. Some of the latter carnivores were actively trapped to increase egg survival, thus enhancing bird populations. The National Audubon Society, National Geographic Magazine and the California Department of Fish and Game view it as a role model illustrating how a refinery turned land used to treat industrial effluents back into native habitat. Planted near the mouth of San Pablo Bay in Richmond in the late '80s, the restored wetland grows typical California marsh plants including salt marsh bulrush, cattail and rabbitfoot grass.

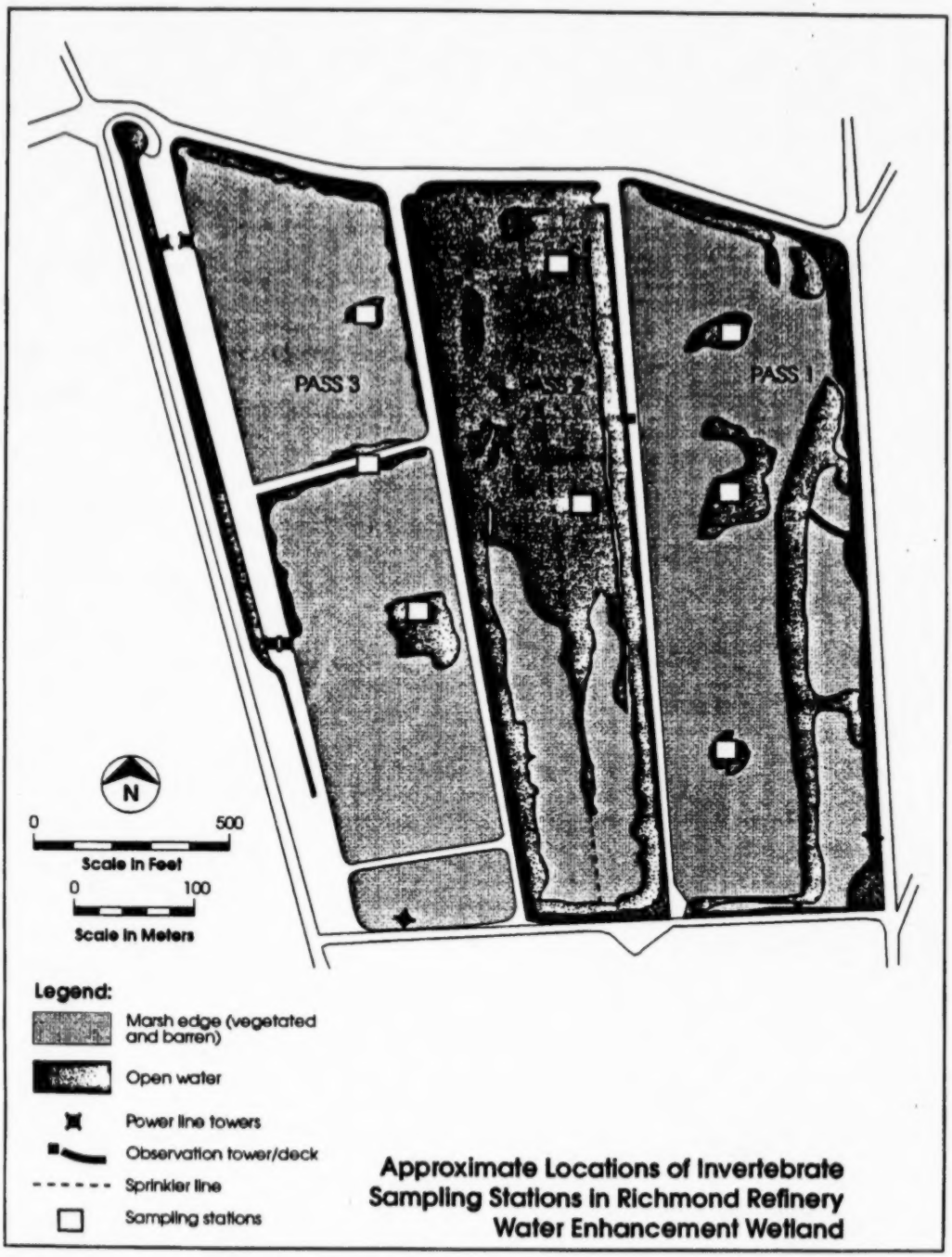

Figure 11. Layout of the Chevron refinery wetland treatment system. Taken from 45.

Se is taken up by organisms living in the wetlands. Se concentrations reach 31.0 µg/dry g in midge larvae (*Chironomus* species), 17.3 µg/dry g in water boatmen and 12.8 µg/dry g in snails (45). These concentrations are twice those predicted from invertebrates living in Tulare Basin evaporation ponds, apparently reflecting the fact that selenate is found in these ponds. Interestingly, tissue Se concentrations do not reflect ambient dissolved Se concentrations, but correlate with the average Se concentrations from the previous 2-3 weeks.

The U.S. Fish and Wildlife Service is concerned that Se is accumulating in the wetlands and causing toxic effects. Se concentrations in black-neck stilt eggs average (geometric mean) 20.4 µg/dry g, a concentration predicted to result in non-viability and/or embryonic deformations (45). These concentrations have increased the rate of deformities in young birds to an estimated 10-30%, whereas the rate of deformities is expected to be less than 1% (46).

To mitigate impacts of Se toxicity on bird populations, Chevron modified the treatment wetland by densely planting the first two passes and modifying their shoreline, both to deter bird usage. These passes was further altered to remain continually submerged, thereby improving treatment performance and preventing accidental drying out of sediments and release of accumulated selenium. Finally, the last pass was modified to enhance bird usage. The result of these modifications is that treatment efficiency is maintained, while selenium content in bird eggs decreased dramatically (47).

Unfortunately, no cost information is available for this system. However, the author's experience suggests that such a system would cost between $1-3 million to design and construct (depending on topography, soils, flow control structures, etc), and approximately $100,000/year to operate (including monitoring costs) and maintain. Such a system could accept up to 2,000 gpm (454 m^3/hr), removing 80-95% of input Se, depending on flows. Operation in a Northern climate would be seasonal, with water stored in an impoundment or reservoir during the winter.

4.3.4 *Natural Attenuation in Evaporation Ponds*

Microalgae and submerged aquatic plants can volatilize significant quantities of selenium from the water column. This ability has been exploited in California to remove Se from contaminated agricultural drainage. Drainage entering the Hacienda Evaporation Basin of the Tulare Lake Drainage District, Corcoran, CA, shows a progressive decrease in Se concentrations despite becoming more concentrated due to water evaporation. Rates of volatilization from planktonic algae for selenium concentrations of 1 µg/g are 220 ng/hour (48). These rates are achieved when conditions in the pond are favorable for plant growth and activity, which include slightly alkaline pH, clear water, non-limiting nutrient (i.e., nitrogen and phosphorus) concentrations, etc. Nevertheless, a retention time of approximately 80 days is sufficient to remove Se completely from agricultural drainage.

Unfortunately, these evaporation basins have caused reproductive impacts to avocets feeding and nesting at these sites. The operators of these basins have modified the design and management of the basins to discourage shorebird use and nesting (49). Modified designs include: greater water depths, steep banks with 3:1 slopes, no islands or windbreaks, level bottoms, and plastic lined or "stacked" rip-rap banks for erosion control. Management strategies include rapid filling and drawdowns of the ponds, intensive hazing during the pre-breeding and breeding seasons, vegetation control on the banks and ponds, and clean, smooth, scraped dikes and banks. Hazing efforts include: propane cannons, cracker shells, bird bombs, mylar flagging, airboat, and vehicles. Other management strategies include modifying sites adjacent to the basin that attracted birds to the basin area or providing a freshwater mitigation wetland adjacent to the evaporation basin. These mitigation efforts have succeeded in reducing bird use and, consequently, Se-induced reproductive failures.

5 Discussion

The chemical properties of selenium help explain several aspects of selenium treatment. Thus, the relatively greater reactivity of selenite (Se(IV)) compared with selenate (Se(VI)) (similarly to the greater reactivity of sulphite compared with sulphate) explains why iron precipitation will readily remove selenite from solution but not selenate.

Any of the technologies reviewed above could be used at the coal mines in West-Central Alberta, but they may not all be well suited. To compare their relative suitability, these technologies are assessed using the criteria listed below[8].

1. Achievable discharge concentrations (12 points)
2. Cost-effectiveness (12 points)
3. Treatment for selenate (8 points)
4. Operational constraints (i.e., land area or power requirement, temperature-dependence, by-product disposal, etc) (8 points)
5. Operational experience, reliability of the technology (6 points)
6. Post-treatment management (Brine disposal, sludge storage/management) (6 points)
7. Maturity of the technology (bench-, pilot-, or full-scale experience) (6 points)
8. Volumes of water that can be treated (4 points)
9. Development time (2 points)

The highest score is given when a criterion is completely met (e.g., effluent Se is 5 μg/L or less) or a technology is best suited (e.g., most cost-effective, requires no post-treatment management of residues). Each technology is assigned points for each criterion, and the technology with the highest score is recommended as that best suited for the coal mines in West-Central Alberta. Operational constraints are factored in Item 4, arising mainly from the long, cold winters and limited availability of flat areas existing at these coal mines. In some cases, professional judgment was applied when there was little or no information to evaluate a technology under a specific criterion.

The results of this evaluation are presented in Table 6. It must be borne in mind that this is a generic evaluation conducted without site-specific information. There may be circumstances at a mine that favour one option over another.

[8] The rationale for the scores assigned to each criterion is as follows. Costs and achievable discharge concentrations are the most important selection criteria by companies and government, respectively. Selenate treatability is important, but a chemical reduction step to selenite, which adds operational complexity and costs, can be used if selenate treatment is poor. Operational experience, post-treatment management, and maturity of the technology are somewhat less important – they are not make-or-break factors – but they are still quite significant in evaluating a technology. Some technologies can only handle limited flows, which handicaps them and should be considered in this evaluation. Finally, a minor issue is the time it takes to develop a technology for a site: development times of two month are preferred over two years.

Table 6. Evaluation of selenium treatment technologies for suitability to Alberta coal mines.

	Achievable[1] discharge [Se]	Cost-effectiveness	Selenate treatability	Operational constraints[3]	Experience, reliability	Post Manag't	Maturity	Water Volume	Dev't Time	Total Score
Maximum Points[2]	**12**	**12**	**8**	**8**	**6**	**6**	**6**	**4**	**2**	**64**
Reverse Osmosis	12	2	7	7	6	2	6	2	2	**46**
Nanofiltration	12	6	8	7	5	2	2	2	2	**46**
Ion exchange	8	2	3	8	3	1	1	2	2	**30**
Iron precipitation	3	4	2	7	5	2	5	4	1	**33**
Catalyzed cementation	3	2	3	6	1	3	2	2	1	**23**
Algal volatilization	5	12	6	3	2	6	2	3	1	**40**
Biological treatment plant	12	8	8	7	5	5	5	2	1	**53**
In-situ	12	12	8	5	3	5	2	4	1	**52**
Biopass system	10	10	8	3	4	4	2	2	1	**44**
Treatment wetlands	10	10	8	2	4	4	3	3	1	**45**
Evaporation ponds	6	12	6	2	2	3	2	3	1	**37**

[1] Headings correspond to categories identified in Page 27.
[2] Maximum possible score for each category.
[3] See discussion on Page 27.

Two technologies stand out from the others: In-situ treatment and Bioreactors (biological treatment plant). Both technologies score well with regards to effluent selenium concentrations and cost-effectiveness. Unlike filtration methods, treatment wetlands or evaporation ponds, these technologies can also operate in cold climates without heating. These two technologies appear to be most suitable for coal mines in West-Central Alberta. The fact that biological treatment systems have been favoured in the past five years undoubtedly reflects the above results.

Several consultants have indicated during the interviews that In-situ treatment is the method of choice *if applicable at a site*. As such, it is one of the technologies to consider first. Its applicability is dependent on favourable subsurface conditions.

Bioreactors have proved to be more reliable than expected in treating selenium, as well as a number of other contaminants. Another unexpected characteristic is their apparently good treatment efficiency at cold temperatures (e.g., 2-4 °C). There are now four biological treatment plants that remove selenium in the USA, suggesting that this technology is becoming more mature. Note that they are located in Western states (e.g., South Dakota, Montana), where winters are comparable with those of West-Central Alberta.

Four other technologies form a second group in the ranking: reverse osmosis, nanofiltration, the Biopass/passive treatment systems and treatment wetlands. These technologies might possibly be appropriate to some of the sites if favoured by some site-specific factors, e.g., suitable land is available for treatment wetland or inexpensive equipment or other factor reduces the cost for RO treatment. Passive technologies, such as the Biopass system or treatment wetlands, might be favoured over others if several dispersed small flows require treatment, if they contribute significant loadings of selenium to receiving waters, and if their continued collection after mine closure proves onerous.

Treatment plants using iron precipitation could be suitable for waters containing low selenite concentrations. However, this does not seem to be the case for the coal mines where selenium speciation has been investigated.

The remaining technologies are too underdeveloped or inappropriate for application in West-Central Alberta.

It should be noted that preventative measures will always be preferred over treatment systems, at least for long-lasting contaminant leaching. Presently, there is not enough information to determine if Se release is a short-term or long-term problem in West-Central Alberta. This is an important issue that should be evaluated since evidence from other mines suggests that it might be a long-term problem. The most common preventative measures were only briefly described above and were not evaluated. However, there is a substantial body of literature that addresses such reclamation techniques, one of which was mentioned earlier[1].

In summary, this evaluation concludes that the two best treatment technologies are in-situ treatment and bioreactors (biological treatment plant), because they can remove selenium down to acceptable levels cost-effectively, even during cold winters comparable to those in West-Central Alberta. Four other technologies – reverse osmosis, nanofiltration, the Biopass/passive treatment systems and treatment wetlands – merit consideration and may be appropriate in certain circumstances at West-Central Alberta coal mines. Notwithstanding the advantages or disadvantages of each technology, preventative measures to minimize selenium release should be implemented as an integral component of any management plan at these mines.

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Appendix I

Topics used for questions during study

Topics used for questions during study

1. Characteristics of the water to be treated
    a. Selenium concentrations; selenite vs selenate
    b. Other constituents, such as nitrate, sulphate, or TDS that might affect treatment performance
    c. Other contaminants for which treatment is required
    d. Flows
2. Description of the treatment system
    a. Necessary pre-treatment
    b. Selenium removal process
    c. Post-treatment
    d. Treatment performance/discharge criteria
    e. Seasonal vs year-round treatment
3. Years of operation
4. Operational issues
    a. Stability of performance
    b. Seasonal/temperature effects, if relevant
    c. Maintenance issues
5. Costs
    a. Capital
    b. Any savings from using available equipment
    c. Operational cost, broken down, if possible
6. Time required for system development

Appendix II

List of people contacted during study

List of people contacted during study

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19. Ross Smart, Senior Scientist, ChevronTexaco R&D Co. Richmond, CA, USA. Tel: (510) 242-2914.

20. Bill Schafer, President, Schafer Ltd. Bozeman MN, USA. Tel: (406) 587-6100.

21. Mark Strosher, BC Ministry of Environment, Lands, and Parks (MELP). Cranbrook, BC. Tel: (250) 489-8522.

22. Leslie Thompson, V.-P. Research, Pintail Systems. Golden, CO, USA. Tel: (303) 642-3520.

23. Rory Tibbals, Operations Superintendent, Golden Sunlight Mine, Placer-Dome Ltd. Whitehall, MN, USA. Tel: (406) 287-2046.

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